BENZENE

Identified as a toxic air contaminant under California's air toxics program (AB 1807) in 1984.

CAS Registry Number: 71-43-2

Molecular Formula: C_6H_6



Benzene is a clear, colorless, volatile, highly flammable liquid with a characteristic sickly, sweet odor. It is chemically characterized by six carbon atoms linked in a planar symmetrical hexagon (equal C-C bond lengths) with each carbon atom attached to a hydrogen atom. The electronic structure of that geometry makes benzene unusually stable. It does react with other compounds mainly by the substitution of a hydrogen atom (U.S. EPA, 1993b). Benzene is soluble in water and miscible with alcohol, chloroform, ether, carbon disulfide, carbon tetrachloride, glacial acetic acid, acetone, and oils (Merck, 1989).

Physical Properties of Benzene

Synonyms: benzol; benzole; bicarburet of hydrogen; pyrobenzol; cyclohexatriene; annulene; coal naphtha; phene; phenyl hydride

Molecular Weight: 78.11
Boiling Point: 80.1 °C
Melting Point: 5.5 °C

Flash Point: -11.1 °C (closed cup) Vapor Pressure: 100 mm Hg at 26.1 °C

Vapor Density: 2.7 (air = 1) Density/Specific Gravity: 0.8787 at 15/4 °C

Henry's Law Constant, water: 0.0055 atm-m³/mole at 25 °C

Log Octanol/Water Partition Coefficient: 2.13

Conversion Factor: $1 \text{ ppm} = 3.19 \text{ mg/m}^3$

(Howard, 1990; HSDB, 1995; Merck, 1989; Sax, 1989; U.S. EPA, 1994a)

SOURCES AND EMISSIONS

A. Sources

The predominant sources of total benzene emissions in the atmosphere are gasoline fugitive emissions and gasoline motor vehicle exhaust. Mobile sources contribute 85 percent and industry-related stationary sources 15 percent of the emissions. Approximately 70 percent of

mobile source benzene emissions can be attributed to onroad motor vehicles, with the remainder attributed to non-road mobile sources (U.S. EPA, 1993b).

Currently the benzene content of gasoline is 1 to 2 percent. Because of its anti-knock properties, a mixture of benzene-rich aromatics is added to gasoline as a replacement for alkyl lead compounds. Some of the benzene in the fuel is emitted from vehicles as unburned fuel. Benzene is also formed as a partial combustion product of larger complex aromatic fuel components. Non-benzene aromatics in gasoline such as toluene, ethylbenzene, xylenes, and heavy reformate (C_9^+) tend to increase exhaust benzene levels with an average effect, per unit of aromatic content, of about 8 percent of that of benzene in gasoline (Marshall, 1988). Generally, the fraction of benzene in the exhaust hydrocarbons varies from 3 to 5 percent (U.S. EPA, 1993b).

Although benzene is not present in household products except in small amounts in some automotive and cleaning products, it is a widely used industrial chemical. In 1985, it was the 16th highest-volume chemical produced in the United States (Sax, 1987). It is used in the manufacture of medicinal chemicals, shoes, dyes, detergents, explosives, linoleum, oil cloth, and artificial leather. Benzene is a solvent for waxes, fats, resins, paints, plastics, and fast drying inks. Other uses are as a raw material in the synthesis of organic compounds such as cyclohexane, styrene, phenol, and rubber (HSDB, 1995). Tobacco smoke contains benzene (ATSDR, 1991). Benzene emissions occur from agricultural burning, forest management burning, and wildfires. These emissions can vary significantly from year to year (ARB, 1984a).

The primary stationary sources that have reported emissions of benzene in California are crude petroleum and natural gas mining, petroleum refining, and electric services (ARB, 1997b).

B. Emissions

The total emissions of benzene from stationary sources in California are estimated to be at least 870,000 pounds per year, based on data reported under the Air Toxics "Hot Spots" Program (AB 2588) (ARB, 1997b). In 1994, the Air Resources Board (ARB) estimated that approximately 38 million pounds per year were emitted from on-road motor vehicles (ARB, 1995f). The ARB also estimates that emissions from other mobile sources such as off-road recreational vehicles, boats, ships, and trains, contribute an additional 8.7 million pounds per year of benzene into California's air each year (ARB 1995f).

Benzene emissions have been reduced and are expected to be reduced further in California through a progression of regulatory measures, control technologies, and reformulated fuel. Benzene was identified by the ARB as a toxic air contaminant in January 1985. Although Stage II vapor recovery boot nozzles had been in place for volatile organic compound emissions in ozone nonattainment areas to reduce benzene exposure, Stage II vapor recovery boot nozzles have been phased-in at all gasoline stations in California starting in July 1987 (ARB, 1987e). In 1988, the ARB required the use of hold open latches on gasoline-dispensing nozzles as a means

of reducing personal exposure to emissions of benzene (ARB, 1988a). In 1993, diesel fuel regulations were implemented which lowered the aromatic hydrocarbon content of California diesel fuel (ARB, 1988b). In March 1996, California began use of "cleaner burning gasoline" California Phase II reformulated gasoline (CaRFG) statewide. The CaRFG limits the benzene content to 0.8 volume percent on average (ARB, 1992g).

C. Natural Occurrence

Benzene occurs in nature as emissions from volcanos and forest fires, and as a natural constituent of crude oil and plant volatiles (HSDB, 1995).

AMBIENT CONCENTRATIONS

Benzene is routinely monitored in California by the ARB air toxics network. When benzene was formally identified as a toxic air contaminant, the ARB estimated a 1982 population-weighted annual concentration of 14.67 micrograms per cubic meter (μ g/m³) or 4.6 parts per billion (ppb) (ARB, 1984a). The network's mean concentration of benzene from January 1996 through December 1996 is estimated to be 2.26 μ g/m³ or 0.71 ppb (ARB, 1997c).

The United States Environmental Protection Agency (U.S. EPA) has also compiled ambient concentration data from Lima, Ohio during 1990 to 1991. Information from the data showed a mean concentration of 2.56 μ g/m³ (0.78 ppb) with a range of concentrations from 1.10 to 6.75 μ g/m³ (0.34 to 2.08 ppb) (U.S. EPA, 1993a).

INDOOR SOURCES AND CONCENTRATIONS

Indoor benzene sources include tobacco smoke, heating and cooking systems, evaporation from various products used in a home or work area, and drift from outdoor automobile exhaust. Based on the results from all California residential studies to date, the indoor air benzene concentration is about 1.5 times higher than the outdoor air benzene concentration.

The most recent California study measuring benzene, was conducted in Woodland, California in the spring of 1990. The mean concentration of benzene of 124 indoor samples was $4.5 \,\mu \text{g/m}^3$ (1.4 ppb). The geometric mean for personal air benzene was $3.4 \,\mu \text{g/m}^3$ (1.07 ppb). Mean indoor concentrations from the Woodland study are approximately 3.8 times greater than the outdoor mean concentration of $1.2 \,\mu \text{g/m}^3$ (0.38 ppb) from the same study (Sheldon et al., 1992).

The California Total Exposure Assessment Methodology (TEAM) studies were conducted in 1984 and 1987. Los Angeles and Contra Costa County were included in the 1984 study, while Los Angeles was the only area for the 1987 study. Mean indoor benzene concentrations measured in the TEAM studies ranged from 0.28 to 16.4 μ g/m³ (0.09 to 5.14 ppb) (the second lowest mean concentration was 5.15 μ g/m³ or 1.6 ppb); the 90th percentile values ranged from 8.96 to 40.00 μ g/m³ (2.8 to 12.5 ppb). Indoor concentrations were only slightly higher than

outdoor concentrations (Pellizzari et al, 1987b; 1989).

A southern California study measured a mean benzene concentration inside motor vehicles of 42.4 μ g/m³ (13.3 ppb) and a maximum concentration of 266.5 μ g/m³ (83.6 ppb) during the summer of 1987 and winter of 1988 (Shikiya et al., 1989). Similar studies in Raleigh, North Carolina and Boston, Massachusetts measured average concentrations of 11.6 and 17.0 μ g/m³ (3.6 and 5.3 ppb) and maximum concentrations of 42.8 and 64.0 μ g/m³ (13.4 and 20.1 ppb), respectively (Chan et al., 1991a; Chan et al., 1991b). Average in-vehicle benzene concentrations were about 3 to 6 times greater than ambient concentrations during these studies.

ATMOSPHERIC PERSISTENCE

Benzene exists in the atmosphere in the gas phase. The dominant atmospheric loss process for benzene in the troposphere is by reaction with the hydroxyl (OH) radical. Based on this reaction, the atmospheric lifetime and half-life are estimated to be 12 days and 8 days, respectively. The reaction products from this reaction include phenol (with a reported yield of 24 percent), glyoxal and other ring-opened compounds (Atkinson, 1994).

AB 2588 RISK ASSESSMENT INFORMATION

The Office of Environmental Health Hazard Assessment reviews risk assessments submitted under the Air Toxics "Hot Spots" Program (AB 2588). Of the risk assessments reviewed as of April 1996, benzene was the major contributor to the overall cancer risk in 85 of the approximately 550 risk assessments reporting a total cancer risk equal to or greater than 1 in 1 million and contributed to the total cancer risk in 284 of the these risk assessments. Benzene was also the major contributor to the overall cancer risk in 16 of the approximately 130 risk assessments reporting a total cancer risk equal to or greater than 10 in 1 million, and contributed to the total cancer risk in 92 of these risk assessments (OEHHA, 1996a).

For non-cancer health effects, benzene contributed to the total hazard index in 52 of the approximately 89 risk assessments reporting a total chronic hazard index greater than 1. Benzene also contributed to the total hazard index in 5 of the approximately 107 risk assessments reporting a total acute hazard index greater than 1 (OEHHA, 1996b).

HEALTH EFFECTS

Probable routes of human exposure to benzene are inhalation and ingestion of drinking water (U.S. EPA, 1994a).

Non-Cancer: Brief inhalation exposure to high concentrations of benzene can cause central nervous system depression. Acute effects include central nervous system symptoms of nausea, tremors, drowsiness, dizziness, headache, intoxication, and unconsciousness. Benzene vapors are mildly irritating to the eyes and respiratory tract. Benzene can sensitize

the myocardium to the arrythmogenic effects of epinephrine. Chronic human inhalation exposure can cause hematopoietic system decreases in erythrocytes, leukocytes, or platelets with progression to leukopenia, thrombocytopenia, pancytopenia, and/or aplastic anemia (U.S. Federal Register, 1977). Occupational exposures to low concentrations have been observed to have an initial stimulant effect on the bone marrow, followed by aplasia and fatty degeneration. Workers chronically exposed to benzene have shown alterations in serum levels of immunoglobulins (U.S. EPA, 1993b).

Results from several studies conducted in rats and mice have indicated depressed cellular proliferation in the bone marrow from short-term exposures to benzene (U.S. EPA, 1994a). In humans, there have been reports of menstrual disorders and possibly reduced fertility associated with benzene exposure, but these reports are limited by factors such as simultaneous exposure to several chemicals, or poor or no controls. In mice and rats, following inhalation of benzene during pregnancy, reduced fetal weight and other indications of growth retardation have been observed. Exposure of pregnant mice resulted in alterations of hematopoiesis in the fetus or offspring, but no effects on red or white blood cell count or hemoglobin analysis. The significance of the hematopoietic alterations is unclear (ATSDR, 1993e; HSDB, 1994).

A chronic non-cancer Reference Exposure Level (REL) of 71 μ g/m³ is listed for benzene in the California Air Pollution Control Officers Association Air Toxics "Hot Spots" Program, Revised 1992 Risk Assessment Guidelines. The toxicological endpoint considered for chronic toxicity is the central and peripheral nervous system (CAPCOA, 1993). An acute REL is not listed. The Reference Concentration (RfC) and oral Reference Dose (RfD) for benzene are under review by the U.S. EPA (U.S. EPA, 1994a).

Cancer: Increased incidences of leukemias, especially acute myelogenous leukemia and its variants including erythroleukemia and myelomonocytic leukemia, have been observed in humans occupationally exposed to benzene (ARB, 1984a). A retrospective mortality study in China in 1989 has provided supporting evidence that benzene exposure is associated with cancers in humans (Yin, 1989). Animal cancer bioassays show benzene causes leukemia and a variety of other cancers including cancers of the lymphoid system, skin, ovary, oral cavity, lip, tongue, lung, mammary gland, and two secretory organs unique to rodents, the Zymbal and preputial glands (ARB, 1984a).

The U.S. EPA classified benzene in Group A: Human carcinogen based on sufficient epidemiological evidence, and determined an inhalation potency value of 8.3×10^{-6} (microgram per cubic meter)⁻¹. The U.S. EPA estimates that if an individual were to breathe air containing benzene at $0.1 \, \mu \text{g/m}^3$, over a lifetime, that person would theoretically have no more than a 1 in 1 million increased chance of developing cancer (U.S. EPA, 1994a). The International Agency for Research on Cancer (IARC) classified benzene in Group 1: Human carcinogen based on sufficient evidence in humans (IARC, 1987a).

The State of California has determined under Proposition 65 and AB 1807 that benzene

is a carcinogen (CCR, 1996; ARB, 1984a). The inhalation potency factor that has been used as a basis for regulatory action in California is 2.9×10^{-5} (microgram per cubic meter)⁻¹ (OEHHA, 1994). In other words, the potential excess cancer risk for a person exposed over a lifetime to $1 \mu g/m^3$ of benzene is estimated to be no greater than 29 in 1 million. The oral potency factor that has been used as a basis for regulatory action in California is 1.0×10^{-1} (milligram per kilogram per day)⁻¹ (OEHHA, 1994).